EXAMPLE 9

Adhesive bonding to a proprietary metallic alloy containing and/or capable of binding metallic ions, used for both dental and industrial applications, was signifi- 5 cantly stronger when the method of the present invention was used, compared to conventional procedures.

What is claimed is:

- 1. A method for preparing the surface of dentin, enamel, or other natural or industrial substrates containing or capable of binding metallic ions, for adhesion of composite materials or resins, which method comprises:
 - (a) first contacting with the surface an aqueous solution or solutions comprising (1) at least one strong acid and (2) at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N (p-tolyl) glycine and glycidyl methacrylate, (3) the addition reaction product of Nphenylglycine and glycidyl methacrylate, and (4) 20 other amino acids;
 - (b) then contacting with the surface a solution comprising at least one monomer selected from the group consisting of (1) the addition reaction prodyethyl methacrylate, (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, (3) 4-methacryloxyethyltrimellitic anhydride, and (4) other compounds containing at least one group or 30 is nitric acid. moiety capable of free radical polymerization and at least one aromatic ring or moiety containing electron-withdrawing substituents that do not interfere with free radical polymerization.
- 2. A method as in claim 1 wherein the concentration 35 from about 0.1% to a saturated solution. of the strong acid is from about 0.1% to about 50%.
- 3. A method as in claim 1 wherein the concentration of the strong acid is from about 2 to 5%.
- 4. A method as in claim 1 wherein the strong acid is nitric acid.
- 5. A method as in claim 1 wherein the strong acid is phosphoric acid.
- 6. A method as in claim 1 wherein the concentration of the solution comprising at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl) glycine and glycidyl methacrylate, (3) the addition reaction product of Nphenylglycine and glycidyl methacrylate, and (4) other amino acids is from about 0.1% to a saturated solution.
- 7. A method as in claim 1 wherein the concentration of the monomer in the solution of subpart (b) is from about 0.1% to a saturated solution.
- 8. A method as in claim 1 wherein the solvent for the solution of subpart (b) is acetone.
- 9. A method as in claim 1 wherein the aqueous solution of subpart (a) contains compatible organic watersoluble solvents sufficient to maintain the compound or compounds and their strong acid salts in solution.
- 10. A method as in claim 1 wherein the strong acid is 60 nitric acid and the compound of subpart (a)(2) is N-
- 11. A method as in claim 1 wherein the compound of subpart (a)(2) is N-phenylalanine.
- 12. A method for preparing the surface of dentin, 65 enamel, or other natural or industrial substrates containing or capable of binding metallic ions, for adhesion of composite materials or resins, which method comprises:

- (a) first contacting with the surface an aqueous solution or solutions comprising at least one strong acid:
- (b) then contacting with the surface a solution comprising a solvent and at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl)glycine and glycidyl methacrylate, (3) the addition reaction product of N-phenylglycine and glycidyl methacrvlate, and (4) other amino acids; and
- (c) then contacting with the surface a solution comprising at least one monomer selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhyride and 2-hydroxyethyl metherylate, (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, (3) 4methacryloxyethyltrimellitic anhydride, and (4) other compounds containing at least one group or moiety capable of free radical polymerization and at least one aromatic ring or moiety containing electron-withdrawing substituents that do not interefere with free radical polymerization.
- 13. A method as in claim 12 wherein the concentrauct of pyromellitic acid dianhydride and 2-hydrox- 25 tion of the strong acid is from about 0.1% to around 50%.
 - 14. A method as in claim 12 wherein the concentration of the strong acid is from about 2 to 5%.
 - 15. A method as in claim 12 wherein the strong acid
 - 16. A method as in claim 12 wherein the strong acid is phosphoric acid.
 - 17. A method as in claim 12 wherein the concentration of the compound in subpart (b) in the solvent is
 - 18. A method as in claim 12 wherein the concentration of the solution of at least one monomer is from about 0.1% to a saturated solution.
 - 19. A method as in claim 12 wherein the solvent for 40 the solution of subpart (b) is acetone.
 - 20. A method as in claim 12 wherein the solvent for the solution of subpart (c) is acetone.
 - 21. A method for preparing the surface of dentin, enamel, or other natural or industrial substrates contain-45 ing or capable of binding metallic ions, for adhesion of composite materials or resins, which method comprises:
 - (a) first contacting with the surface an aqueous solution or solutions comprising (1) at least one strong acid or acidic salt, (2) at least one polyvalent cation, (3) at least one polyfunctional acid which can form relatively water-insoluble precipitates with calcium or polyvalent cations at pH values above that of the aqueous solution, and (4) at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl) glycine and glycidyl methacrylate, (3) the addition reaction product of N-phenylglycine and glycidyl methacrylate, and (4) other amino acids;
 - (b) then contacting with the surface a solution comprising at least one monomer selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate, (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, (3) 4-methacryloxyethyltrimelliticanhydride, and (4) other compounds containing at least one group or moiety capable of free radical polymerization and